ON THE SECULAR EQUATION IN PERTURBATION THEORY

微擾論中久期方程之研究

by

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CHAPTER I

INTRODUCTION

In the long history of the use of perturbation theory for obtaining approximate solutions of the time-independent Schrödinger equation, many different perturbation expansions have involved, each of which has its own particular advantages in solving particular physical problems.

Recently, two papers were published by Y. W. Chan* on the expansion of a determinant in terms of the cylcic product of its elements. With the aid of that expansion, an implicit formula for the eigenvalues of the determinant in terms of a ratio of two simple series expansions is obtained. The method was then applied to Mathieu's type of secular equations, that is, a secular equation with all matrix elements equal to zero except H_{ii}, $H_{i\,i+h}$ and $H_{i+h\,i}$, where i represents any state and h is a fixed integer. The eigenvalue formula for this particular problem can further be reduced to continued fractions of the matrix elements. The remarkably simple expression provides very accurate results.

The purpose of this dissertation is to apply Chan's method to a more general case, in particular, to a secular equation which can be referred to as 'Four-off-diagonal type', i.e. an equation in which the matrix elements can be expressed as follows:

$$(\alpha,\beta) = H_{\alpha\beta}\left(\delta_{\alpha\beta} + \delta_{\alpha\,\beta-\xi} + \delta_{\alpha\,\beta+\xi} + \delta_{\alpha\,\beta-\xi-\eta} + \delta_{\alpha\,\beta+\xi+\eta}\right) \tag{1}$$

where ξ, η are some fixed positive integers.

Chapter II contains a brief review of Chan's method and a discussion of the possibility of obtaining continued fractions for secular equations which are more complicated than Mathieusequation.

*see Ref. (5),(6)

In Chapter III, the Floquet Hamiltonian of a two-level atom in a classical sinusoidal field, being a special case of the four-off-diagonal type, will be considered as an example for extending the applicability of Chan's continued fraction method.The result obtained will be compared with the works of Muriel*, Sen Gupta**, and Swain***.

In Chapter IV, a general formulation of the implicit equation for solving the eigenvalues of four-off-diagonal type will be derived.

In Chapter V, a second example concerning the eigenvalues of one-dimensional anharmonic oscillator with ax^4 as a perturbed Hamiltonian will be treated. Five energy states will be calculated and compared with those results obtianed by the first and second order perturbation, by the variational method, and by the 'near exact' answers using computer working with a 20 x 20 sub-matrix.

In Chapter VI, discussions for the relation between the sub-matrix size, the order of approximation, and the accuracy of the calculated result will be provided. The Energy eigenvalues of Chapter V are treated as numerical examples of the discussions.

Overall advantages, disadvantages, and the most applicable areas of the above derived general formulation will be discussed in the concluding Chapter of this dissertation.

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*see Ref. (17)

**see Ref. (13)

***see Ref. (20)(21)(22)

CHAPTER II

CHAN'S METHOD ON THE SOLUTION OF SECULAR EQUATION

(A) Expressing eigenvalues of a secular equation in terms of the ratio of two simple series expansions*

In a given linear vector space, eigenvalues E_i of an operator can be found by forming a secular equation:

$$D_n = |H_{kj} - E_i \delta_{kj}| = 0 \quad , \quad k = 1, 2, 3, \ldots, n \tag{1}$$

E_i denotes one of the n solutions of the secular solution, and $H_{kj} = \langle u_k | \mathcal{H} | u_j \rangle$, where u_k, u_j are elements of a orthonormal functions. The eigenfunction Ψ_ω can then be expanded:

$$\Psi_\omega = \sum_j a_{\omega j} u_j \tag{2}$$

Defining the cyclic product,

$$(ijkl \ldots st) = (i,j)(j,k)(k,l) \cdots (s,t)(t,i) \tag{3}$$

where $i \neq j \neq k \neq l \neq m \neq n \neq \ldots s \neq t$,

and also, let

$$\sum_p (ijkl \ldots st) \tag{4}$$

denotes the summation over all possible nonequivalent cyclic permutations.

*Section (A) and (B) are just a brief review of Chan's method. This is needed because it serves as a framework of derivations presented in Chapter IV.

D_n in Eq. (1) can be expanded in terms of a particular index i, using the operation $\sum_p (ijk\ .\ .\ .\ st)$ defined above,

$$\bar{D}_n \equiv \frac{D_n}{\prod_i^n (i)} = \sum_p^{n-1} \left[1 - \frac{(jk)}{(j)(k)} - \frac{(jk\ell)}{(j)(k)(\ell)} - \cdots \right] + \sum_{\neq i\ p}^{n-1} \left[- \frac{(ij)}{(i)(j)} + \frac{(ijk)}{(i)(j)(k)} - \frac{(ijk\ell) - (ij)(k\ell)}{(i)(j)(k)(\ell)} + \cdots \right] \tag{5}$$

By Eq. (5), the implicit solution E_i in Eq. (1) can be expressed by,

$$E_i = H_{ii} - R_i(E_i) \tag{6}$$

where

$$R_i(E_i) \equiv (i) = \frac{\bar{N}_i}{\bar{M}_{ii}^{ii}} \tag{7a}$$

with

$$\bar{N}_i \equiv \sum_{\neq i\ p}^{n-1} \left[\frac{(ij)}{(j)} - \frac{(ijk)}{(j)(k)} + \frac{(ijk\ell) - (ij)(k\ell)}{(j)(k)(\ell)} - \frac{(ijk\ell m) - (ij)(k\ell m) - (ijk)(\ell m)}{(j)(k)(\ell)(m)} + \frac{(ij)(k\ell)(ms) - (ijk\ell)(ms) - (ij)(k\ell ms) + (ijk\ell ms) - (ijk)(\ell ms)}{(j)(k)(\ell)(m)(s)} - \cdots \right] \tag{7b}$$

$$\bar{M}_{ii}^{ii} \equiv \sum_{=\ p}^{n-1} \left[1 - \frac{(jk)}{(j)(k)} + \frac{(jk\ell)}{(j)(k)(\ell)} - \frac{(jk\ell m) - (jk)(\ell m)}{(j)(k)(\ell)(m)} + \frac{(jk\ell ms) - (jk)(\ell ms) - (jk\ell)(ms)}{(j)(k)(\ell)(m)(s)} - \cdots \right] \tag{7c}$$

(B) Derived from Eq. (6), eigenvalues of the secular equation with matrix elements of the form $(\alpha,\beta) = H_{\alpha\beta}\,(\,\delta_{\alpha\beta} + \delta_{\alpha\,\beta-h} + \delta_{\alpha\,\beta+h})$ can be solved in terms of continued fractions

It has been found that a number of physics problems are associated with a secular equation in which all matrix elements are always zero except H_{ii}, $H_{i\,i+h}$, and $H_{i+h\,i}$, where i represents any state and h is a fixed integer, using Kronecker delta notation,

$$(\alpha,\beta) = H_{\alpha\beta}\,(\,\delta_{\alpha\beta} + \delta_{\alpha\,\beta-h} + \delta_{\alpha\,\beta+h}) \tag{8}$$

The immediate consequence of such a matrix is that for all α and β, any cyclic product with more than two indices vanishes, that is,

$$(ijk) = (ijkl) = \ldots = (ijkl\ldots st) = 0 \tag{9}$$

The reason for this is worth noting. The cyclic product is started by a matrix element

$$(i,j) \neq 0 \;, \text{ where } j=i\pm h \;, \tag{10}$$

The following element (j,k) which will be linked with (i,j) to form the cyclic product has only three selections, $(j,j-h)$, (j), and $(j,j+h)$. (j) is excluded according to the definition in Eq. (3). Moreover, from Eq. (8), $(i,j) \neq 0$ implies $(j,j-h) = (j,j+h-h)=(j,i)$ which terminates the cyclic product and thus excluded also.

Therefore, the only possibility for a non-zero (j,k) which links with a non-zero (i,j) to form a cyclic product with more than two indices is

$$(j,k) = (j,j+h) \tag{11}$$

from Eq. (10), $j = i + h$, so that

$$(j,k) = (j,j+h) = (j,i+2h) \tag{12}$$

Applying similar arguments of Eq. (10) (11) (12)

$$\begin{aligned}&(ijkl\ldots st)\\ &=(i,i+h)(i+h,i+2h)(i+2h,i+3h)\ldots(i+\overline{\pi-2}h,i+\overline{\pi-1}h)(i+\overline{\pi-1}h,i)\end{aligned} \tag{13}$$

where π is the number of indices in the cyclic product.

From Eq. (8)

$$(i+\overline{\pi-1}h,i)=0 \quad , \qquad \text{for all } \pi>2$$

Therefore ,

$$(ijkl\ldots st)=0 \quad , \qquad \text{for all } \pi>2 \tag{14}$$

By using the characteristic of Eq. (1~~6~~4), Eq(~~8~~7) can be very much simplified,

$$R_i(E_i)=\frac{N_i}{M_{ii}^{ii}} \tag{15}$$

where,

$$N_i = \sum_{\neq i, P}^{n-1} \left[\frac{(ij)}{(j)} - \frac{(ij)(kl)}{(j)(k)(l)} + \frac{(ij)(kl)(ms)}{(j)(k)(l)(m)(s)} - \cdots \right]$$

$$M_{ii}^{ii} = \sum_{\neq i, P}^{n-1} \left[1 - \frac{(jk)}{(j)(k)} + \frac{(jk)(lm)}{(j)(k)(l)(m)} - \cdots \right]$$

The ratio N/M can be expressed in terms of continued fractions

$$(i) \equiv R_i = \frac{(i\ i-h)}{(i-h)} \Big/ F(i-h) + \frac{(i\ i+h)}{(i+h)} \Big/ F_i(i+h) \tag{16}$$

where

$$F_i(i-h) = 1 - \cfrac{(i-h\ \ i-2h)/(i-h)(i-2h)}{1 - \cfrac{(i-2h\ \ i-3h)/(i-2h)(i-3h)}{1 - \cdots}} \tag{17a}$$

and

$$F_i(i+h) = 1 - \cfrac{(i+h\ \ i+2h)/(i+h)(i+2h)}{1 - \cfrac{(i+2h\ \ i+3h)/(i+2h)(i+3h)}{1 - \cdots}} \tag{17b}$$

E_i can be solved by iteration method. Thus Eq. (16) (17) are the general formula for finding the eigenvalue of any excited state i for those kinds of secular equation in which all matrix elements are always zero except H_{ii}, $H_{i\,i+h}$, and $H_{i+h\,i}$, where h is a fixed integer.

(C) Discussion on CHAN'S series expansion method

(1) Advantages of the method:

(i) It is particularly suitable for those special types of matrices with all non-zero elements clustering around the diagonal

According to this series expansion method, a determinantis expanded by series in terms of particular index i. If D_n is an arbitrary determinant (i.e. its non-zero terms are arbitrarily distributed). This series expansion method is not much better than other methods (e.g. expansion by cofactors). Those (ij), (ijk), (ijkl) . . . etc. terms are still very complicated, and this method can be less efficient than the standard Jacobi Method of diagonalizational routine.* However, the situation is different if the non-zero entries are distributed close to the diagonal. First of all, there are less cyclic products. Secondly, as the non-zero entries are close to the diagonal, the numerical differences between i, j, k, l, . . . are limited. Moreover, as the necessary condition for the existence of (ijkl . . . st) is that (t,i) is not equal to zero, and as the numerical difference between t and i is limited, those (i,j),(j,k),(k,l) . . . terms are bounded to be clustered around the index i. We have therefore the following feature for any cyclic product with fixed total number π of indices in the cyclic product: only those elements close to the index i are involved. Thus no matter how the size of the matrix is extended, the number of non-zero fixed π cyclic products is still unchanged.

Compared with other detail diagonalization methods, larger index i (or, higher excited state) involves a

* see Reference (7).

larger sized matrix (at least ixi in size), which is more and more complicated to diagonalize. With our present method, no matter what the index i is, we consider only a small sub-matrix block with center (i). The later method is clearly simpler.

(ii) When the method is applied to Mathieu's Type of secular equation (i.e. $(\alpha,\beta) = H_{\alpha\beta}(\delta_{\alpha\beta} + \delta_{\alpha\,\beta-h} + \delta_{\alpha\,\beta+h})$)

By using Eq. (16)(17), the 6th excited state eigenvalue of Mathieu's equation was calculated by Chan*. The result was compared with other different methods provided by Feenberg* and Sasakawa**. Error for Feenberg's method is 1.45634, for Sasakawa's method is 0.07781, and for Chan's method, possible error is only ±0.00002.

(2) Limitation of the Method

(i) The limitation for reducing the ratio of series into continued fraction

The possibility of using continued fraction depends on two criteria. First, (ijkl . . . st) = 0, for all $\pi > 2$ which derived from Eq. (14). For if non-zero (ijkl . . . st) exists, Eq. (15) connot be obtained. Secondly, we can see from Eq. (15) that for any index j, there can at most be two associated k, with one of them being i which generates that very j. Moreover, criteria for l associated with k . . . etc. are similar, if there exist more than two k (e.g. $k_1, k_2 \neq i$) associated with j, two l (e.g. l_1, l_2) associated with k.

$$\frac{N_i}{M_{ii}} = \frac{\dfrac{(i\,j)}{(j)}}{1 - \dfrac{(j k_1)}{(j)(k_1)} \sum_p \left[1 - \dfrac{(l_1 m_1)}{(l_1)(m_1)} - \dfrac{(l_2 m_1)}{(l_2)(m_1)} - \cdots\right] - \dfrac{(j k_2)}{(j)(k_2)} \sum_p \left[1 - \dfrac{(l_1 m_1)}{(l_1)(m_1)} - \dfrac{(l_2 m_1)}{(l_2 m_1)} - \cdots\right]}$$

$$= \frac{(ij)/(j)}{1 - \dfrac{(jk_1)/(j)(k_1)}{1 - \dfrac{(k_1 l_1)/(k_1)(l_1)}{1 - \cdots} - \dfrac{(k_1 l_2)/(k_1)(l_2)}{1 - \cdots}} - \dfrac{(jk_2)/(j)(k_2)}{1 - \dfrac{(k_2 l_1)/(k_2)(l_1)}{1 - \cdots} - \dfrac{(k_2 l_2)/(k_2)(l_2)}{1 - \cdots}}} \tag{18}$$

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*see Ref. (16).
**see Ref. (5).

The continued fraction application is failed.

(ii) For higher excited states (i.e. index i is larger, F(i-h) in Eq. (17a) becomes more and more complicated. In other words, F(i-h) continued fraction cannot desirably trucked, and must alternatively count indices backward until

$$(s,t)=(i-(i-h),\ i-i)=(h,0) \tag{19}$$

The reason is that for lower value of index s, t (st)/ (s) (t) is larger and bears significant weight for the accuracy of the result. For very higher excited state (e.g. $i > 30$), F(i-h) is extremely complicated for exact consideration. Thus we came to a dilemma. If we want a simpler method for solving the eigenvalue, we have to cut off some later terms in the continued fraction F(i-h), and yet, the result is poorer.

CHAPTER III

APPLYING CHAN'S METHOD FOR SOLVING THE SCHRÖDINGER EQUATION WITH A HAMILTONIAN PERIODIC IN TIME

(A) Interaction of a two-level quantum system with an oscillating field in a formalism with a time-independent Hamiltonian represented by an infinite matrix*.

There are several physical situations which involve a quantum system with two discrete states, connected by an oscillating interaction. Physical examples of this kind of systems are spin one-half particle in a static magnetic field with an oscillating magnetic field at frequency ω applied perpendicularly to the static field. Other instances are the semiclassical description of an RF resonance measurement on a doublet excited state formalism** and the Bloch-Siegert shift†.

Let the amplitudes for the system of states α and β be $a_\alpha(t)$ and $a_\beta(t)$, the energies E_α and E_β , the Schrödinger equation ($\hbar = 1$),

$$i\frac{d}{dt}\begin{pmatrix} a_\alpha(t) \\ a_\beta(t) \end{pmatrix} = \begin{pmatrix} E_\alpha & 2b\cos\omega t \\ 2b\cos\omega t & E_\beta \end{pmatrix}\begin{pmatrix} a_\alpha(t) \\ a_\beta(t) \end{pmatrix} \qquad (1)$$

where b is real.

*The floquet Hamiltonian derived below is a summary of the work done by Shirley (see Ref. 18)

**see Ref. (19)

†see Ref. (22)

By Floquet's theorem and Fourier expansion, the Floquet Hamiltonian of Eq.(1) is,

$$H^{(F)}=\begin{pmatrix} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\ \cdot & E_\beta-2\omega & b & 0 & 0 & 0 & 0 & 0 & 0 & \cdot \\ \cdot & b & E_\alpha-\omega & 0 & 0 & b & 0 & 0 & 0 & \cdot \\ \cdot & 0 & 0 & E_\beta-\omega & b & 0 & 0 & 0 & 0 & \cdot \\ \cdot & 0 & 0 & b & E_\alpha & 0 & 0 & b & 0 & \cdot \\ \cdot & 0 & b & 0 & 0 & E_\beta & b & 0 & 0 & \cdot \\ \cdot & 0 & 0 & 0 & 0 & b & E_\alpha+\omega & 0 & 0 & \cdot \\ \cdot & 0 & 0 & 0 & b & 0 & 0 & E_\beta+\omega & b & \cdot \\ \cdot & 0 & 0 & 0 & 0 & 0 & 0 & b & E_\alpha+2\omega & \cdot \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \end{pmatrix} \tag{2}$$

Defining $\omega_0 \equiv E_\alpha - E_\beta$, in the case of two-state system in a strong oscillating field $E_\alpha=\frac{1}{2}\omega_0$ and $E_\beta=-\frac{1}{2}\omega_0$, (3)

the secular equation for finding the Floquet exponent q is

$$\left| H^{(F)}_{kj} - q_i\,\delta_{kj} \right| = 0 \tag{4}$$

(B) <u>Implicit expression for q in Eq.(4) by Chan's series expansion method</u>

The Floquet Hamiltonian $H^{(F)}$ in Eq.(2) is not belong to the Mathieu's type which was mentioned in Section B, Chapter II. But rather, it is a more complicated one which we can call the four-off-diagonal type, and its elements can be expressed as,

$$(\alpha,\beta) = H_{\alpha\beta}\left(\delta_{\alpha\beta} + \delta_{\alpha\,\beta-\xi} + \delta_{\alpha\,\beta+\xi} + \delta_{\alpha\,\beta-\xi-\eta} + \delta_{\alpha\,\beta+\xi+\eta}\right) \tag{5}$$

where ξ, η are some fixed integers.

But as the zero terms of the four-off-diagonals are regularly arranged, the matrix elements can be expressed by a simpler form as the following:

$$(\alpha,\beta)=\begin{cases} H_{\alpha\beta}\left(\delta_{\alpha\beta} + \delta_{\alpha\,\beta+\xi+\eta} + \delta_{\alpha\,\beta-\xi}\right) & \text{where } \alpha \text{ is odd} \quad (6a) \\ H_{\alpha\beta}\left(\delta_{\alpha\beta} + \delta_{\alpha\,\beta+\xi} + \delta_{\alpha\,\beta-\xi-\eta}\right) & \text{where } \alpha \text{ is even} \quad (6b) \end{cases}$$

and $H_{\alpha\beta}=b$, $\alpha\neq\beta$, $\xi=1$, $\eta=2$ (6c)

"Odd" is taken arbitrarily (for $H^{(F)}$ is an infinite matrix) to be the index of the row in $H^{(F)}$ which involves E_β.

By the similar argument of Eq. (9)-(14), Chapter II, let the cyclic product (ijkl . . .st) is started by $(i,j) \neq 0$, for example*, take $j = i+\xi+\eta$, the associated element (j,k) has three possibilities, i. e. $(j,j-\xi-\eta)$, (j,j), $(j,j+\xi)$. From Eq. (6b), $(i,j)\neq 0$ implies $(j,j-\xi-\eta)=(j,(i+\xi+\eta)-\xi-\eta)$ (j,i), which terminates the cyclic product. Thus the only selection for (i,j) where $j=i+\xi+\eta$ is $k=j+\xi=i+2\xi+\eta$, furthermore, $l=i+3\xi+2\eta$, $m=i+4\xi+2\eta$, $n=i+5\xi+3\eta$. . ., it is increasing in numerical value, and therefore (ijkl. . .st) equals to zero for $\pi>2$, the direct implication of such characteristics is the reduced formula Eq. (15) or Eq. (17), Chapter II.

As $H^{(F)}$ is an infinite matrix, every element inside the sub-matrix concerned must be labelled by some indexing system before applying Eq. (15). For convenience, E_α in $H^{(F)}$ of Eq. (2) is labelled as (i,i).

Applying Chan's expansion method to $H^{(F)}$ for the implicit expression of q with index i, we find**

$$
\begin{aligned}
(i) &= \frac{N^{(i)}}{M^{(i)}} \\
&= \left\{ \frac{(i\ i-\xi)}{(i-\xi)} \sum_{\neq i, i-\xi} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \frac{(kl)(mS)}{(k)(l)(m)(s)} \cdots \right] + \frac{(i\ i+\xi+\eta)}{(i+\xi+\eta)} \sum_{\substack{\neq i, \\ i+\xi+\eta}} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \frac{(kl)(ms)}{(k)(l)(m)(s)} \cdots \right] \right\} \\
&\quad \times \left\{ \sum_{\neq i} {}_P \left[1 - \frac{(jk)}{(j)(k)} + \frac{(jk)(ml)}{(j)(k)(m)(l)} \cdots \right] \right\}^{-1}, \\
&= \frac{(i\ i-\xi)}{(i-\xi)} \sum_{\neq i, i-\xi} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \cdots \right] \times \left\{ \sum_{\neq i, i-\xi} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \cdots \right] - \frac{(i-\xi\ i-\xi-\eta)}{(i-\xi-\eta)(i-\xi)} \sum_{\substack{\neq i, i-\xi \\ i-\xi-\eta}} {}_P \left[1 - \frac{(lm)}{(l)(m)} + \cdots \right] \right\}^{-1} \\
&\quad + \frac{(i\ i+\xi+\eta)}{(i+\xi+\eta)} \sum_{\substack{\neq i, \\ i+\xi+\eta}} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \cdots \right] \times \left\{ \sum_{\substack{\neq i, \\ i+\xi+\eta}} {}_P \left[1 - \frac{(kl)}{(k)(l)} + \cdots \right] - \frac{(i+\xi+\eta\ \ i+\xi+\eta+\xi)}{(i+\xi+\eta)(i+\xi+\eta+\xi)} \sum_{\substack{\neq i, \\ i+\xi+\eta, i+\xi+\eta+\xi}} {}_P \left[1 - \frac{(lm)}{(l)(m)} + \cdots \right] \right\}^{-1} \\
&= \mathcal{F}^{(-)} + \mathcal{F}^{(+)}
\end{aligned}
\tag{7a}
$$

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*Same argument for the cases when $j=i+\xi$, $i-\xi$, $i-\xi-\eta$

**From Ref. (18), we know that the eigenvalues $\lambda_{\alpha n} = g_\alpha + n\omega$, where $g_\alpha = \lambda_{\alpha 0}$ is chosen to be the smallest absolute value, thus if we start with indices other than i, the results only differ by $n\omega$, where n=1,2,3. . .

For the purpose of convenience*, we let i=10 , then by the same procedures stated in Section(B), Chapter III.

$$\mathcal{F}^{(-)} = \cfrac{(10\ 9)/(9)}{1 - \cfrac{(9\ 6)/(9)(6)}{1 - \cfrac{(6\ 5)/(6)(5)}{1 - \cfrac{(5\ 2)/(5)(2)}{\ddots}}}} \tag{7b}$$

$$\mathcal{F}^{(+)} = \cfrac{(10\ 13)/(13)}{1 - \cfrac{(13\ 14)/(13)(14)}{1 - \cfrac{(14\ 17)/(14)(17)}{1 - \cfrac{(17\ 18)/(17)(18)}{\ddots}}}} \tag{7c}$$

Now we have $E_\alpha=\frac{1}{2}\omega_c$, $E_\beta=-\frac{1}{2}\omega_c$, Eq.(7) becomes

$$\frac{1}{2}\omega_c - \mathcal{E} = \cfrac{b^2/(-\frac{1}{2}\omega_c-\omega-\mathcal{E})}{1 - \cfrac{b^2/(-\frac{1}{2}\omega_c-\omega-\mathcal{E})(\frac{1}{2}\omega_c-2\omega-\mathcal{E})}{1 - \cfrac{b^2/(\frac{1}{2}\omega_c-2\omega-\mathcal{E})(-\frac{1}{2}\omega_c-3\omega-\mathcal{E})}{1 - \cfrac{b^2/(-\frac{1}{2}\omega_c-3\omega-\mathcal{E})(\frac{1}{2}\omega_c-4\omega-\mathcal{E})}{\ddots}}}}$$

$$+ \cfrac{b^2/(-\frac{1}{2}\omega_c+\omega-\mathcal{E})}{1 - \cfrac{b^2/(-\frac{1}{2}\omega_c+\omega-\mathcal{E})(\frac{1}{2}\omega_c+2\omega-\mathcal{E})}{1 - \cfrac{b^2/(\frac{1}{2}\omega_c+2\omega-\mathcal{E})(-\frac{1}{2}\omega_c+3\omega-\mathcal{E})}{1 - \cfrac{b^2/(-\frac{1}{2}\omega_c+3\omega-\mathcal{E})(\frac{1}{2}\omega_c+4\omega-\mathcal{E})}{\ddots}}}} \tag{8}$$

*i can equal to any integer, e.g. i=0. Number ten is assigned because of avoiding negative indices.

After arrangements,

$$q = \frac{1}{2}\omega_c + b^2 \left(\cfrac{1}{q+\frac{1}{2}\omega_c-\omega-\cfrac{b^2}{q-\frac{1}{2}\omega_c-2\omega-\cfrac{b^2}{q+\frac{1}{2}\omega_c-3\omega-\cfrac{b^2}{q-\frac{1}{2}\omega_c-4\omega-\cdots}}}} + \cfrac{1}{q+\frac{1}{2}\omega_c+\omega-\cfrac{b^2}{q-\frac{1}{2}\omega_c+2\omega-\cfrac{b^2}{q+\frac{1}{2}\omega_c+3\omega-\cfrac{b^2}{q-\frac{1}{2}\omega_c+4\omega-\cdots}}}} \right) \quad (9)$$

Many authors have concerned with the solutions of Eq. (4). Muriel† has presented a solution to the Liouville equation, while Sen Gupta* has criticized as being inconsistent with the Floquet theorem which provided by Whittaker and Watson in 1914, and he also concerned with the wave function other than eigenvalues. In a recent development, Swain** published three articles, obtaining the exact solution by using difference equation. The most interesting feature is that his results concerning this problem is exactly the same as Eq. (9), but from a completely different method.

C) Discussion

The derivation developed in the last section illustrates an extension of Chan's continued fraction method which can apply not only to the Mathieu's tupe, but also to the special case of Four-off-diagonal type with some characteristics similar to those in Mathieu's type. We can summarize the criteria and generalize it to the situation not only for two-off-diagonal type (e.g. Mathieu's type) of secular equation but also for all kinds of matrices with the following characteristics:

(i) The elements of the matrix appear in pairs, i.e. for all non-zero (α,β) there exists an associated non-zero (β,α) (but not necessarily $(\alpha,\beta) = (\beta,\alpha)$ as in the case of symmetric matrix.)

*see Ref. (13) † see Ref. (17)
**see Ref. (20)(21)(22)

(ii) The elements of the matrix can be expressed by

$$(\alpha,\beta) = H_{\alpha\beta}(\delta_{\alpha\beta} + \delta_{\alpha\mu} + \delta_{\alpha\gamma}) \tag{10}$$

where $(\alpha-\mu)$, $(\gamma-\alpha)$ are positive integers. And the implicit solution of these kind can be expressed by

$$(i) = \mathcal{F}^{(-)}(i) + \mathcal{F}^{(+)}(i) \tag{11}$$

where $\mathcal{F}^{(-)}(i)$ and $\mathcal{F}^{(+)}(i)$ are continued fractions similar to Eq. (7b), (7c) which are obtained by using successive series grouping and dividing developed in Eq. (15), Chapter II.

CHAPTER IV

GENERAL IMPLICIT FORMULATION FOR THE FOUR-OFF-DIAGONAL TYPE OF SECULAR EQUATION

(A) Difficulties arised in general four-off-diagonal type of secular equation*

As defined in Chapter III section (B), the four-off-diagonal type are secular equations whose elements can be expressed by

$$(\alpha,\beta)=H_{\alpha\beta}(\delta_{\alpha\beta}+\delta_{\alpha\,\beta-\xi}+\delta_{\alpha\,\beta+\xi}+\delta_{\alpha\,\beta-\xi-\eta}+\delta_{\alpha\,\beta+\xi+\eta}) \qquad (1)$$

where ξ, η are some fixed positive integers.

There exist at least two different kinds of difficulties, because of which the solution cannot be expressed as an implicit equation in continued fractions.

(1) The existnece of non-zero cyclic product (ijkl. . .st)

Apart from the characteristics which was derived in section (B) of the last chapter (p.4), we see that in case there exist five non-zero elements (including the diagonal element) for each column, the cyclic products (ijkl. . .st) with $\pi > 2$ are not necessarily equal to zero. A non-zero cyclic product will occur whenever the following criterion is satisfied,

$$(i-j)+(j-k)+(k-l)+\cdots+(s-t)(t-i)=0 \qquad (2)$$

where (i,j),(j,k),(k,l) . . . are non-zero elements. It then follows that the continued fraction method, which applied to Mathieu's type of secular equation fails in this case.

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*Four-off-diagonal type of secular equation occurs in many areas of Physics, e.g. Shirley's Floquet Hamiltonian which is discussed in Chapter III, anharmonic oscillators with ax^3, ax^4 as perturbed Hamiltonian.

(2) Even if cyclic products (ijkl . . .st) are all equal to zero. By the argument in Chapter II, section (B), (2)(i), for any index i, from Eq. (1) there exists 4 different non-zero (i,j). By Eq. (18), Chapter II, the continued fraction method again fails.

(3) Failing to perform a reduction to continued fractions, we must go back to the general formula, Eq. (7), Chapter II, and directly evaluate the operator $\sum_p$. It is in general quite complicated to find all the permutations contained in $\sum_p$ when the number of indices involved is large. However, the procedure may be simplified somewhat for a secular equation of the Four-off-diagonal type.

(B) <u>Simplify $\sum_p(ij)(kl)(mn)\ldots(st)$ and $\sum_p(ijkl\ldots st)$</u>

From Eq. (1) we have five non-zero elements in every row i. Thus for every i, there are four corresponding values of j such that $(i,j)\neq 0$, that is,

$$j = i+\alpha \tag{3}$$

where $\alpha = -\xi-\eta\,,\ -\xi\,,\ \xi\,,\ \xi+\eta$

Let $\{\xi,\eta\}$ denotes the dummy variable α taking values $-\xi-\eta$, $-\xi$, ξ, and $\xi+\eta$. Then

$$\sum_{\neq i}^{n-1}{}_p\,(ij) = \sum_{\alpha=\{\xi,\eta\}}(i\ \ i+\alpha) \tag{4}$$

For the case $\sum_p(ij)(kl)\ldots(st)$, a similar derivation can be obtained, except for one more constraints,

$$\sum_{\neq i}^{n-1}{}_p\,(ij)(kl)\ldots(st) \tag{5}$$
$$= \sum_{\omega=\{\xi,\eta\}}{}'\sum_{\psi=\{\xi,\eta\}}{}'\cdots\sum_{\beta=\{\xi,\eta\}}{}'\sum_{\alpha=\{\xi,\eta\}}{}'(i\ \ i+\alpha)(i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)\cdots(i+\alpha+\beta+\cdots\psi\ \ \ i+\alpha+\beta+\cdots\psi+\omega)$$

where $\alpha,\beta,\cdots,\psi,\omega$ are dummy variables and $\sum'$ is defined as the summation of all dummy variables for those cases when $i\neq i+\alpha\neq\cdots\neq i+\alpha+\beta+\cdots+\psi+\omega$

For $\sum_p(ijkl\ldots st)$, define the summation operator $\sum''$ by two conditions:

i) $i\neq i+\alpha\neq i+\alpha+\beta\neq\cdots\neq i+\alpha+\beta+\cdots+\psi\neq i+\alpha+\beta+\cdots+\psi+\omega$ (6)

ii) $|\alpha+\beta+\cdots+\psi+\omega|\leqslant 2(\xi+\eta)$ (7)

Then,

$$\sum_{\neq i}^{n-1}{}_{P}(ijkl\cdots st)=\sum_{\omega=\{\xi,\eta\}}''\sum_{\psi=\{\xi,\eta\}}''\cdots\sum_{\beta=\{\xi,\eta\}}''\sum_{\alpha=\{\xi,\eta\}}''(i\ \overline{i+\alpha}\ \overline{i+\alpha+\beta}\cdots\overline{i+\alpha+\beta+\cdots+\psi+\omega}) \tag{8}$$

(C) <u>General implicit formulation for four-off-diagonal type of secular equation</u>

By using Eq.(5) and Eq.(8), Eq.(7), Chapter II, can formally be expressed as follows, (up to 3rd order of approximation*)

$$(i)=\frac{\mathcal{N}_i}{\mathcal{M}_{ii}^{ii}} \tag{9a}$$

where

$$\mathcal{N}_i=\sum_{\neq i}^{n-1}{}_{P}\left[\frac{(ij)}{(j)}-\frac{(ijk)}{(j)(k)}+\frac{(ijkl)-(ij)(kl)}{(j)(k)(l)}-\cdots\right]$$

$$=\sum_{\alpha=\{\xi,\eta\}}'\frac{(i\ i+\alpha)}{(i+\alpha)}-\sum_{\beta=\{\xi,\eta\}}''\sum_{\alpha=\{\xi,\eta\}}''\frac{(i\ \ i+\alpha\ \ i+\alpha+\beta)}{(i+\alpha)(i+\alpha+\beta)}$$

$$+\sum_{\gamma=\{\xi,\eta\}}''\sum_{\beta=\{\xi,\eta\}}''\sum_{\alpha=\{\xi,\eta\}}''\frac{(i\ \ i+\alpha\ \ i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)}$$

$$-\sum_{\gamma=\{\xi,\eta\}}'\sum_{\beta=\{\xi,\eta\}}'\sum_{\alpha=\{\xi,\eta\}}'\frac{(i\ \ i+\alpha)(i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)}$$

$$-\sum_{\beta=\{\xi,\eta\}}{}^{\prime *}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}{}^{\prime *}\sum_{\alpha=\{\xi,\eta\}}{}^{\prime *}\frac{(i\ \ i+\alpha)(i+\alpha'\ \ i+\alpha'+\beta)}{(i+\alpha)(i+\alpha')(i+\alpha'+\beta)}$$

$$-\sum_{\gamma=\{\xi,\eta\}}{}^{\prime *}\sum_{\beta=\{\xi,\eta\}}{}^{\prime *}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}{}^{\prime *}\sum_{\alpha=\{\xi,\eta\}}{}^{\prime *}\frac{(i\ \ i+\alpha)(i+\alpha'+\beta\ \ i+\alpha'+\beta+\gamma)}{(i+\alpha)(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)}+\cdots \tag{9b}$$

$$\mathcal{M}_{ii}^{ii}=\sum_{\neq i}^{n-1}{}_{P}\left[1-\frac{(jk)}{(j)(k)}+\frac{(jkl)}{(j)(k)(l)}-\cdots\right]$$

$$=1-\sum_{\beta=\{\xi,\eta\}}'\sum_{\alpha=\{\xi,\eta\}}'\frac{(i+\alpha\ \ i+\alpha+\beta)}{(i+\alpha)(i+\alpha+\beta)}$$

$$-\sum_{\gamma=\{\xi,\eta\}}{}^{\prime *}\sum_{\beta=\{\xi,\eta\}}{}^{\prime *}\sum_{\alpha=\{\xi,\eta\}}{}^{\prime *}\frac{(i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha+\beta)(i+\alpha+\beta+\gamma)}$$

$$+\sum_{\gamma=\{\xi,\eta\}}''\sum_{\beta=\{\xi,\eta\}}''\sum_{\alpha=\{\xi,\eta\}}''\frac{(i+\alpha\ \ i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)}-\cdots \tag{9c}$$

$\sum^{*}$ denotes all the repetitions which have already occurred in other summation terms are excluded.

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*The order of approximation is defined as the power of the unknown eigenvalue which is involved in the equation.

For 4th order of approximation, adding terms for Eq. (9) in the numerator is,

$$\begin{aligned}
&\sum_{\epsilon=\{\xi,\eta\}}^{\prime\prime}\sum_{\gamma=\{\xi,\eta\}}^{\prime\prime}\sum_{\beta=\{\xi,\eta\}}^{\prime\prime}\sum_{\alpha=\{\xi,\eta\}}^{\prime\prime}\Big[(i\;\; i+\alpha)(i+\alpha+\beta\;\; i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)\\
&\quad+(i\;\; i+\alpha\;\; i+\alpha+\beta)(i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)-(i\;\; i+\alpha\;\; i+\alpha+\beta\;\; i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)\Big]\\
&\quad\times\Big[(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)(i+\alpha+\beta+\gamma+\epsilon)\Big]^{-1}\\
&+\sum_{\gamma=\{\xi,\eta\}}^{*\prime\prime}\sum_{\beta=\{\xi,\eta\}}^{*\prime\prime}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}^{*\prime\prime}\sum_{\alpha=\{\xi,\eta\}}^{*\prime\prime}\Big\{\frac{(i\;\; i+\alpha)(i+\alpha'\;\; i+\alpha'+\beta\;\; i+\alpha'+\beta+\gamma)}{(i+\alpha)(i+\alpha')(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)}\\
&\quad+\frac{(i\;\; i+\alpha\;\; i+\alpha+\beta)(i+\alpha'+\beta\;\; i+\alpha'+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)}\Big\}\\
&+\sum_{\epsilon=\{\xi,\eta\}}^{*\prime\prime}\sum_{\gamma=\{\xi,\eta\}}^{*\prime\prime}\sum_{\beta=\{\xi,\eta\}}^{*\prime\prime}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}^{*\prime\prime}\sum_{\alpha=\{\xi,\eta\}}^{*\prime\prime}\Big\{\frac{(i\;\; i+\alpha)(i+\alpha'+\beta\;\; i+\alpha'+\beta+\gamma\;\; i+\alpha'+\beta+\gamma+\epsilon)}{(i+\alpha)(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)(i+\alpha'+\beta+\gamma+\epsilon)}\\
&\quad+\frac{(i\;\; i+\alpha\;\; i+\alpha+\beta)(i+\alpha'+\beta+\gamma\;\; i+\alpha'+\beta+\gamma+\epsilon)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha'+\beta+\gamma)(i+\alpha'+\beta+\gamma+\epsilon)}\Big\}\\
&+\sum_{\beta=\{\xi,\eta\}}^{*\prime\prime}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}^{*\prime\prime}\sum_{\alpha=\{\xi,\eta\}}^{*\prime\prime}\frac{(i\;\; i+\alpha\;\; i+\alpha+\beta)(i+\alpha'\;\; i+\alpha'+\beta)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha')(i+\alpha'+\beta)}
\end{aligned}\tag{10a}$$

Adding terms for Eq. (9) in the denominator is,

$$\begin{aligned}
&\sum_{\epsilon=\{\xi,\eta\}}^{\prime}\sum_{\gamma=\{\xi,\eta\}}^{\prime}\sum_{\beta=\{\xi,\eta\}}^{\prime}\sum_{\alpha=\{\xi,\eta\}}^{\prime}\frac{(i+\alpha\;\; i+\alpha+\beta)(i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)(i+\alpha+\beta+\gamma+\epsilon)}\\
&-\sum_{\epsilon=\{\xi,\eta\}}^{\prime\prime}\sum_{\gamma=\{\xi,\eta\}}^{\prime\prime}\sum_{\beta=\{\xi,\eta\}}^{\prime\prime}\sum_{\alpha=\{\xi,\eta\}}^{\prime\prime}\frac{(i+\alpha\;\; i+\alpha+\beta\;\; i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)(i+\alpha+\beta+\gamma+\epsilon)}\\
&+\sum_{\beta=\{\xi,\eta\}}^{*\prime}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}^{*\prime}\sum_{\alpha=\{\xi,\eta\}}^{*\prime}\frac{(i+\alpha\;\; i+\alpha+\beta)(i+\alpha'\;\; i+\alpha'+\beta)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha')(i+\alpha'+\beta)}\\
&+\sum_{\epsilon=\{\xi,\eta\}}^{*\prime}\sum_{\gamma=\{\xi,\eta\}}^{*\prime}\sum_{\beta=\{\xi,\eta\}}^{*\prime}\sum_{\substack{\alpha'\neq\alpha\\=\{\xi,\eta\}}}^{*\prime}\sum_{\alpha=\{\xi,\eta\}}^{*\prime}\Big\{\frac{(i+\alpha\;\; i+\alpha+\beta)(i+\alpha'+\beta\;\; i+\alpha'+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)}\\
&\quad+\frac{(i+\alpha+\beta\;\; i+\alpha+\beta+\gamma)(i+\alpha'+\beta\;\; i+\alpha'+\beta+\gamma)}{(i+\alpha+\beta)(i+\alpha+\beta+\gamma)(i+\alpha'+\beta)(i+\alpha'+\beta+\gamma)}\\
&\quad+\frac{(i+\alpha\;\; i+\alpha+\beta)(i+\alpha'+\beta+\gamma\;\; i+\alpha'+\beta+\gamma+\epsilon)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha'+\beta+\gamma)(i+\alpha'+\beta+\gamma+\epsilon)}\\
&\quad+\frac{(i+\alpha+\beta\;\; i+\alpha+\beta+\gamma)(i+\alpha'+\beta+\gamma\;\; i+\alpha'+\beta+\gamma+\epsilon)}{(i+\alpha+\beta)(i+\alpha+\beta+\gamma)(i+\alpha'+\beta+\gamma)(i+\alpha'+\beta+\gamma+\epsilon)}\\
&\quad+\frac{(i+\alpha+\beta+\gamma\;\; i+\alpha+\beta+\gamma+\epsilon)(i+\alpha'+\beta+\gamma\;\; i+\alpha'+\beta+\gamma+\epsilon)}{(i+\alpha+\beta+\gamma)(i+\alpha+\beta+\gamma+\epsilon)(i+\alpha'+\beta+\gamma)(i+\alpha'+\beta+\gamma+\epsilon)}\Big\}
\end{aligned}\tag{10b}$$

Although Eq. (10) is a rather cumbersome expression, in fact many terms occurred in the summation expressions are repeated and cancelled. Thus in real applications, cyclic products involved are limited. But it still puts a considerable constraint to the order of approximation.*

* Numerical illustrations will be shown in Chapter V and VI.

CHAPTER V

APPLICATION TO AN ANHARMONIC OSCILLATOR WITH ax^4 AS PERTURBATION

(A) Introduction

In this chapter, we are going to study the anharmonic oscillator with ax^4 as p rturbed Hamiltonian by applying Eq. (9), Chapter IV, which is the generalized formula for Four-off-diagonal type of secular equation. The results are compared with variational method which was done by McWeeny and Coulson*, first and second order perturbation which diverged and failed, and near exact solution by matrix diagonalization of a 20x20 Hamiltonian matrix**.

The choice of quartic perturbation anharmonic oscillator is not only for illustrative interest, but it also bears physical significance.

The generalized anharmonic oscillator can be defined by the Hamiltonian

$$\hat{H}_m = \frac{\hat{P}^2}{2\mu} - \frac{1}{2}kx^2 + \lambda x^{2m} \qquad m = 2, 3, \cdots \tag{1}$$

The situation becomes more and more complicated for larger m . The most interesting and solvable case which has Physical implication is m=2. Such a simple but important problem has attracted the attention of both field theorists and the chemists.†

* see Ref. (7)

** see Ref. (2)(7)

† see Ref. (3)(4)(12)(8)(9)(10)(11)(7)

(B) The Secular Equation for Quartic Anharmonic Oscillator

We are dealing with the Schrödinger Equation

$$\hat{\mathcal{H}}\,\Phi(x) = E\,\Phi(x) \tag{2}$$

where

$$\hat{\mathcal{H}} \equiv \frac{\hat{p}^2}{2\mu} - \frac{1}{2}kx^2 + ax^4$$

matrix elements of the Hamiltonian are expressed as follows,

$$\mathcal{H}_{n,n} = a\left(\frac{\hbar}{2\mu\omega}\right)^2 3(2n^2+2n+1) + (n+\tfrac{1}{2})\hbar\omega \tag{3a}$$

$$\mathcal{H}_{n,n-2} = \mathcal{H}_{n-2,n} = a\left(\frac{\hbar}{2\mu\omega}\right)^2 2(2n-1)\sqrt{n(n-1)} \tag{3b}$$

$$\mathcal{H}_{n,n-4} = \mathcal{H}_{n-4,n} = a\left(\frac{\hbar}{2\mu\omega}\right)^2\sqrt{n(n-1)(n-2)(n-3)} \tag{3c}$$

where $\omega^2 \equiv k/\mu$

For the sake of comparing the results, we are going to use the notations of Chan, Stelman, and Thompson by defining the following relations:

$$X_\alpha \equiv (4\mu k'/\hbar^2)^{1/4}x \tag{4a}$$

$$\hat{P}_\alpha \equiv (4/\mu\hbar^2 k')^{1/4}\hat{p} \tag{4b}$$

where $k' \equiv k + (a^2\hbar^2/\mu)^{1/3}$ (4c)

The Hamiltonian $\mathcal{H}$ in Eq. (2) is reduced to

$$\hat{\mathcal{H}} = \left\{(k\hbar^2/16\mu) + (a\hbar^2/64\mu^2)^{2/3}\right\}^{1/2}\left\{\hat{P}_\alpha^2 + (1-\alpha)X_\alpha^2 + \alpha^{3/2}X_\alpha^4\right\} \tag{5}$$

α, which may be considered as a measure of the harmonicity of the potential well, is defined as follows

$$\alpha \equiv \frac{(a^2\hbar^2/\mu)^{1/3}}{\{k + (a^2\hbar^2/\mu)^{1/3}\}} \tag{6}$$

The calculation of energy eigenvalues by Four-off-diagonal type method requires the numerical values of

$$\rho \equiv a\left(\frac{\hbar}{2\mu\omega}\right)^2 \tag{7a}$$

$$t \equiv \frac{1}{2}\hbar\omega \tag{7b}$$

Chan, Stelman, and Thompson used the reduced Hamiltonian in Eq. (5) in the unit of $\{(k\hbar^2/16\mu)+(a\hbar^4/64\mu^2)^{2/3}\}^{1/2}$, thus

$$(k\hbar^2/16\mu)+(a\hbar^4/64\mu^2)^{2/3} = 1 \tag{8}$$

or, in terms of ρ and t,

$$\frac{t^2}{4}-\left(\frac{\rho t^2}{4}\right)^{2/3} = 1 \tag{9}$$

Also from Eq. (6)

$$\frac{\alpha}{1-\alpha}=\left(\frac{2\rho}{t}\right)^{2/3} \tag{10}$$

For practical interest, for example, in trimethylene oxide, α is of the order 0.2.
Solving Eq. (9), (10) with $\alpha=0.2$, gives

$$\rho = 0.1117894 \tag{11a}$$

$$t = 1.7886318 \tag{11b}$$

(C) <u>General Implicit Formula for Eigenvalue of Excited State i of Quartic Anharmonic Oscillator derived from Eq. (9), Chapter IV</u>

From Eq. (3) we know that the secular equation for quartic anharmonic oscillator is Four-off-diagonal type, thus Eq. (9) in Chapter IV is applicable with

$$\xi = \eta = 2 \tag{12}$$

For easier operations, we make a little transformation on dummy variables,

$$\begin{aligned}&\sum_{\gamma=\{\xi,\eta\}}{}' \sum_{\beta=\{\xi,\eta\}}{}' \cdots \sum_{\alpha=\{\xi,\eta\}}{}' (i \;\; i+\alpha)\cdots(i+\alpha+\cdots+\beta \quad i+\alpha+\cdots+\beta+\gamma)\\ &=\sum_{\substack{K=-2\\ \neq 0}}^{K=2} \sum_{\substack{\tau=-2\\ \neq 0}}^{\tau=2} \cdots \sum_{\substack{\sigma=-2\\ \neq 0}}^{\sigma=2} (i \;\; i+2\sigma)\cdots(i+2\sigma+\cdots+2\tau \quad i+2\sigma+\cdots+2\tau+2\end{aligned} \tag{13}$$

Also by inspection, we find that non-zero cyclic-products occurs quite regularly,

$$\sum_{\beta=\{\xi,\eta\}}'' \sum_{\alpha=\{\xi,\eta\}}'' \frac{(i\ \ i+\alpha\ \ i+\alpha+\beta)}{(i+\alpha)(i+\alpha+\beta)} = \frac{(i\ \ i\pm2\ \ i\mp2)}{(i\pm2)(i\mp2)} + \frac{2(i\ \ i\pm2\ \ i\pm4)}{(i\pm2)(i\pm4)} \tag{14a}$$

$$\sum_{\gamma=\{\xi,\eta\}}'' \sum_{\beta=\{\xi,\eta\}}'' \sum_{\alpha=\{\xi,\eta\}}'' \frac{(i\ \ i+\alpha\ \ i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)} = \frac{2(i\ \ i\pm2\ \ i\mp2\ \ i\mp4)}{(i\pm2)(i\mp2)(i\mp4)} + \frac{2(i\ \ i\pm2\ \ i\pm6\ \ i\pm4)}{(i\pm2)(i\pm4)(i\pm6)} \tag{14b}$$

$$\sum_{\gamma=\{\xi,\eta\}}'' \sum_{\beta=\{\xi,\eta\}}'' \sum_{\alpha=\{\xi,\eta\}}'' \frac{(i+\alpha\ \ i+\alpha+\beta\ \ i+\alpha+\beta+\gamma)}{(i+\alpha)(i+\alpha+\beta)(i+\alpha+\beta+\gamma)} = \frac{4(i\pm2\ \ i\pm4\ \ i\pm6)}{(i\pm2)(i\pm4)(i\pm6)} + \frac{2(i\pm4\ \ i\pm6\ \ i\pm8)}{(i\pm4)(i\pm6)(i\pm8)} \tag{14c}$$

Substituting Eq. (12),(13),(14) into Eq. (9), Chapter IV, we get the implicit formula for eigenvalue of any excited state up to third order of approximation,

$$(i) = \frac{\bar{N}^i}{\bar{M}^i} \tag{15a}$$

$$\begin{aligned}
\bar{N}^i = {} & \sum_{\substack{\sigma=-2\\ \neq 0}}^{\sigma=2} \frac{(i\ \ i+2\sigma)}{(i+2\sigma)} - \left\{ \frac{(i\ \ i\pm2\ \ i\mp2)}{(i\pm2)(i\mp2)} + \frac{2(i\ \ i\pm2\ \ i\pm4)}{(i\pm2)(i\pm4)} - \frac{2(i\ \ i\pm2\ \ i\mp2\ \ i\mp4)}{(i\pm2)(i\mp2)(i\mp4)} \right. \\
& \left. - \frac{2(i\ \ i\pm2\ \ i\pm6\ \ i\pm4)}{(i\pm2)(i\pm6)(i\pm4)} \right\} - \sum_{\substack{K=-2\\ \neq 0}}^{2}{}' \sum_{\substack{\tau=-2\\ \neq 0}}^{2}{}' \sum_{\substack{\sigma=-2\\ \neq 0}}^{2}{}' \frac{(i\ \ i+2\sigma)(i+2\sigma+2\tau\ \ i+2\sigma+2\tau+2K)}{(i+2\sigma)(i+2\sigma+2\tau)(i+2\sigma+2\tau+2K)} \\
& - \sum_{\substack{\tau=-2\\ \neq 0}}^{2}{}^{*} \sum_{\substack{\sigma'=-2\\ \neq 0,\sigma}}^{2}{}^{*} \sum_{\substack{\sigma=-2\\ \neq 0}}^{2}{}^{*} \frac{(i\ \ i+2\sigma)(i+2\sigma'\ \ i+2\sigma'+2\tau)}{(i+2\sigma)(i+2\sigma')(i+2\sigma'+2\tau)} \\
& - \sum_{\substack{K=-2\\ \neq 0}}^{2} \sum_{\substack{\tau=-2\\ \neq 0}}^{2} \sum_{\substack{\sigma'=-2\\ \neq 0,\sigma}}^{2} \sum_{\substack{\sigma=-2\\ \neq 0}}^{2} \frac{(i\ \ i+2\sigma)(i+2\sigma'+2\tau\ \ i+2\sigma'+2\tau+2K)}{(i+2\sigma)(i+2\sigma'+2\tau)(i+2\sigma'+2\tau+2K)}
\end{aligned} \tag{15b}$$

$$\begin{aligned}
\bar{M}^i = {} & 1 - \sum_{\substack{\tau=-2\\ \neq 0}}^{2} \sum_{\substack{\sigma=-2\\ \neq 0}}^{2} \frac{(i+2\sigma\ \ i+2\sigma+2\tau)}{(i+2\sigma)(i+2\sigma+2\tau)} + \frac{4(i\pm2\ \ i\pm4\ \ i\pm6)}{(i\pm2)(i\pm4)(i\pm6)} \\
& + \frac{2(i\pm4\ \ i\pm6\ \ i\pm8)}{(i\pm4)(i\pm6)(i\pm8)} - \sum_{\substack{K=-2\\ \neq 0}}^{2} \sum_{\substack{\tau=-2\\ \neq 0}}^{2} \sum_{\substack{\sigma=-2\\ \neq 0}}^{2} \frac{(i+2\sigma+2\tau\ \ i+2\sigma+2\tau+2K)}{(i+2\sigma+2\tau)(i+2\sigma+2\tau+2K)}
\end{aligned} \tag{15c}$$

(D) First Five Energy States Calaulated by Eq. (15)*

1) Ground State: 7x7 sub-matrix, 3rd order of approximation

$$(0)=\frac{\frac{(02)}{(2)}+\frac{(04)}{(4)}-\frac{2(024)}{(2)(4)}+\frac{2(0462)}{(2)(4)(6)}-\frac{(02)(46)}{(2)(4)(6)}-\frac{(04)(26)}{(2)(4)(6)}}{1-\frac{(24)}{(2)(4)}-\frac{(46)}{(4)(6)}-\frac{(26)}{(2)(6)}-\frac{2(246)}{(2)(4)(6)}}$$

By Eq. (3), (7)

$$(2.124-E_0)=\frac{\frac{0.8997736}{(2)}+\frac{0.3}{(4)}-\frac{5.6327724}{(2)(4)}-\frac{134.93224}{(2)(4)(6)}}{1-\frac{29.392643}{(2)(4)}-\frac{181.45455}{(4)(6)}-\frac{4.4988738}{(2)(6)}}$$

where

$$(2)\equiv 13.302945-E_0$$

$$(4)\equiv 29.847782-E_0$$

$$(6)\equiv 51.75851-E_0$$

E_0 can be solved by iteration method**, or by the aid of computer, which is

$$E_0=2.0426068$$

2) First Excited State: 8 x 8 sub-matrix, 3rd order of approximation

$$(1)=\frac{\frac{(13)}{(3)}+\frac{(15)}{(5)}-\frac{2(135)}{(3)(5)}+\frac{[2(1375)-(13)(75)-(15)(37)]}{(3)(5)(7)}}{1-\frac{(35)}{(3)(5)}-\frac{(37)}{(3)(7)}-\frac{(57)}{(5)(7)}-\frac{2(357)}{(3)(5)(7)}}$$

By Eq. (3), (7)

$$(7.0427364-E_1)=\frac{N_1}{M_1}$$

$$N_1=\frac{7.4981231}{(3)}+\frac{1.4996245}{(5)}-\frac{60.351168}{(3)(5)}-\frac{2266.8645}{(3)(5)(7)}$$

---

*The appropriate choice of sub-matrix size and order of approxiation, defining as the power of unknown energy E which is involved in the equation, that will be discussed in Chapter VI.

**see Ref. (7)

$$M_1 = 1 - \frac{80.979718}{(3)(5)} - \frac{10.497375}{(3)(7)} - \frac{354.81113}{(5)(7)} + \frac{1098.3913}{(3)(5)(7)}$$

where

$(3) \equiv 20.904627 - E_1$
$(5) \equiv 40.132409 - E_1$
$(7) \equiv 60.726083 - E_1$

the solution is $E_1 = 6.5111061$

3) <u>Second Excited State</u>: 7 x 7 sub-matrix, 3rd order of approximation

$$(2) = \frac{\frac{(20)}{(0)} - \frac{(24)}{(4)} - \frac{(26)}{(6)} - \frac{2(204)}{(0)(4)} - \frac{2(246)}{(4)(6)} - \frac{[(20)(46)+(26)(40)-(2046)-(2640)]}{(0)(4)(6)}}{1 - \frac{(04)}{(0)(4)} - \frac{(46)}{(4)(6)}}$$

By Eq. (3), (7)

$$(13.302945 - E_2) = \frac{N_2}{M_2}$$

$$N_2 = \frac{0.8997736}{(0)} + \frac{29.392643}{(4)} + \frac{4.4988738}{(6)} - \frac{5.6327724}{(0)(6)} - \frac{309.80265}{(4)(6)} - \frac{134.93224}{(0)(4)(6)}$$

$$M_2 = 1 - \frac{0.3}{(0)(4)} - \frac{181.45455}{(4)(6)}$$

where

$(0) \equiv 2,124 - E_2$
$(4) \equiv 29.847782 - E_2$
$(6) \equiv 51.75851 - E_2$

the solution is $E_2 = 11.6526828$

4) <u>Third Excited State</u>: 8 x 8 sub-matrix, 3rd order of approxiamtion

$$(3) = \frac{\frac{(31)}{(1)} + \frac{(35)}{(5)} + \frac{(37)}{(7)} - \frac{2(315)}{(1)(5)} - \frac{2(357)}{(5)(7)} - \frac{[2(3157)-(31)(57)-(37)(51)]}{(1)(5)(7)}}{1 - \frac{(15)}{(1)(5)} - \frac{(57)}{(5)(7)}}$$

By Eq. (3), (7)

$$20.904627 - E_3 = \frac{N_3}{M_3}$$

$$N_3 = \frac{7.4981231}{(1)} + \frac{80.979718}{(5)} + \frac{10.497375}{(7)} - \frac{60.351168}{(1)(5)} - \frac{1098.3913}{(5)(7)} - \frac{2266.8645}{(1)(5)(7)}$$

$$M_3 = 1 - \frac{1.4996245}{(1)(5)} - \frac{354.81113}{(5)(7)}$$

where

$$(1) \equiv 7.0427364 - E_3$$
$$(5) \equiv 40.132409 - E_3$$
$$(7) \equiv 64.726083 - E_3$$

the solution is $E_3 = 17.2580346$

5) <u>Fourth Excited State:</u> 9 x 9 sub-matrix, 3rd order of approximation

$$(4) = \left\{ \frac{(40)}{(0)} + \frac{(42)}{(2)} + \frac{(46)}{(6)} + \frac{(48)}{(8)} - \frac{2(402)}{(0)(2)} - \frac{2(426)}{(2)(6)} - \frac{2(468)}{(6)(8)} - \frac{(48)(20)}{(0)(2)(8)} - \frac{(40)(68)}{(0)(6)(8)} + \frac{[2(4026)-(40)(26)-(46)(20)]}{(0)(2)(6)} \right.$$
$$\left. + \frac{[2(4268)-(42)(68)-(48)(62)]}{(2)(6)(8)} \right\} \times \left\{ 1 - \frac{(02)}{(0)(2)} - \frac{(26)}{(2)(6)} - \frac{(68)}{(6)(8)} \right\}^{-1}$$

By Eq. (3), (7)

$$29.847782 - E_4 = \frac{N_4}{M_4}$$

$$N_4 = \frac{0.3}{(0)} + \frac{29.392643}{(2)} + \frac{181.45455}{(6)} + \frac{20.994742}{(8)} - \frac{5.6327724}{(0)(2)} - \frac{309.80265}{(2)(6)}$$
$$- \frac{3098.0263}{(6)(8)} - \frac{134.93224}{(0)(2)(6)} - \frac{15962.503}{(2)(6)(8)} - \frac{18.820515}{(0)(2)(8)} - \frac{188.96537}{(0)(6)(8)}$$

$$M_4 \doteq 1 - \frac{0.8997736}{(0)(2)} - \frac{4.4988738}{(2)(6)} - \frac{629.84224}{(6)(8)}$$

where

$$(0) \equiv 2.124 - E_4$$
$$(2) \equiv 13.302945 - E_4$$
$$(6) \equiv 51.75851 - E_4$$
$$(8) \equiv 79.035129 - E_4$$

the solution is $E_4 = 23.4199882$

(E) Comparison of the results with first, second order perturbation, variational method, and exact answers

TABLE 1

RESULTS OF PERTURBATION THEORY, VARIATIONAL METHOD*, FOUR-OFF-DIAGONAL TYPE METHOD, AND EXACT ANSWER** FOR QUARTIC ANHARMONIC OSCILLATOR (α=0.2)

Energy State	Variational Method	1st Order Perturbation	2nd Order Perturbation	Exact	Four-off diagonal type method
0	2.04810	2.124	1.977	2.04270	2.0426068
1	6.52795	7.043	5.890	6.51051	6.5111061
2	11.62670	13.300	9.007	11.62920	11.6526828
3	17.20250	20.900	9.901	17.2332	17.2580346
4	23.17400	29.850	7.148	23.2391	23.4199882

The perturbation method is a complete failure here. Furthermore, the work of Bazley and Fox*** concerning the upper bounds and lower bounds for eigenvalues also point out the inadequacies of the perturbation approach even for small anharmonicities, they showed that second-order perturbation theory gives quite good results for extremely small anharmonicities, but becomes no better than the first order perturbation as the harmonicity is increased.

From TABLE 1, our present method gives quite satisfactory results, the errors being less than one per-cent. Even more remarkably, these results are more accurate than those obtained by the variational method (except for the fourth excited state). Worse fitting for the fourth excited state can be explained by the discussions of Chapter VI: for 9 x 9 sub-matrix the highest order of approximation is up to four. Our present work applies to third order only.

*see Ref. (7)

**see Ref. (7)

***see Ref. (2)

Thus , with respect to two of the most common methods for solving eigenvalue problems (i.e. perturbation and variational method). our present method compares favourably in simplicity and accuracy.

CHAPTER VI

DISCUSSION ON RELATIONS BETWEEN THE SUB-MATRIX SIZE, THE ORDER OF APPROXIMATION, AND THE ACCURACY OF THE RESULT

In this Chapter, we are going to disciss the relations between the sub-matrix size and the order of approximation. Two questions will be concerned: what will be the accuracy of the result if we extend the sub-matrix size with fixed order of approximation? What will happen if we fix the sub-matrix size and extend the order of approximation?

A) <u>The relation between the minimum sub-matrix size and the highest order of approximation</u>

From Eq.(9), Chapter IV, for n th order of approximation terms requires at least n differnet indices to form the cyclic products. The minimum differnece between two adjacent indices is ξ, thus the largest and smallest indices is differed by $n\xi$. So we conclude that the smallest sub-matrix size $\mathcal{A}$ for n th order of approximation is

$$\mathcal{A} = n\xi + 1 \tag{1}$$

Reversely, the maximum order of approximation for the sub-matrix of size $\mathcal{A}$ is

$$n = \frac{\mathcal{A} - 1}{\xi} \tag{2}$$

B) <u>The Accuracy of the result when the order of approxiamtion is increasing with fixed sub-matrix size.</u>

If we fix the sub-matrix to a certain size $\mathcal{A}$, higher order of approximation would give more accurate results. For when the approximation order $n < (\mathcal{A}-1)/\xi$, many terms of Eq.(9)Chap.IV are unconsidere and the case can be referred to as 'unsaturated'.

Choosing the ground state energy eigenvalues of quartic anharmonic oscillator which was discussed in the last chapter as an example, a few numerical results are illustrated in TABLE 2 by fixing the size of the sub-matrix to be 9 x 9.

TABLE 2

Calculation of ground state energy by extending the order of approximation with fixed sub-matrix size

(submatrix size = 9 x 9)

ORDER OF APPROXIMATION	EIGENVALUES	EXACT
2nd	2.0018395	
3rd	2.0486082	2.04270
4th	2.0424238	

C) The Accuracy of the result when the sub-matrix size is increasing with fixed order of approximation

For a certain fixed order of approximation, the accuracy are not necessarily better as we arbitrarily increase the size of the sub-matrix. Rather, the results become worse as the sub-matrix size is larger than $(n\xi+1)$ for nth order of approximation. For it leaves $(n+1)$th, $(n+2)$th , . . . order of approximations unconsidered, which may compensate lower orders of terms to provide a better approxiamtion.

Here we choose the first excited state of quartic anharmonic oscillator as an illustrative example. A few numerical results are illustrated in TABLE 3 by fixing the approximation to the second order.

TABLE 3

Calculation of first excited state energy by extending the sub-matrix size with fixed order of approximation

(order of approximation = 2)

SUB-MATRIX SIZE	EIGENVALUES	EXACT
6 X 6	6.51322743	
8 X 8	6.36259828	6.51051
10 X 10	6.06083932	

The result of 6 x 6 sub-matrix size gives quite accurate answers because it is the smallest sub-matrix size second order of approxiamtion*. In the case of 8 x 8 and 10 x 10, the order of approximations are 'saturated'; and worse results are obtained as the sub-matrix size is increased.

In conclusion, we note that a suitable choice of the sub-matrix size and the order of approxiamtion is important to the accuracy of the result. The idealest case: the order of approximation is $(\mathcal{A}-1)/\xi$ for $\mathcal{A}\times\mathcal{A}$ sub-matrix**. Larger order of approximation for higher excited states calculations are needed.

*By Eq. (1)

**Or equivalently, the sub-matrix size is $n\xi+1$ for nth order of approximation.

CHAPTER VII

CONCLUSION

In this dissertation, we have extended Chan's continued fraction method for solving Mathieu's type of secular equation to Four-off-diagonal type. Shirley's Floquet Hamiltonian of two-level atom in classical sinusiodal field and quartic anharmonic oscillator are treated as an illustrative application as well as physical interests. The results are quite satisfactory.

In comparison with Chan's continued method, we have pointed out the complexity. Yet, it is explanable because Four-off-diagonal type is much more complicated than Mathieu's type, and provides larger areas of physical interest as well.

The limitation of approximation order restricts the method for lower energies calculations. For highly excited states, our formula can serve as rough estimation only.

Secular equation of Six-off-diagonal type, Eight-off-type etc. can be treated by procedures similar to those provided in this dissertation. But as expected it becomes more and more complicated, and the merits of our method will disappear.

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